ing constants of fluorescein and iodide ions is accurately described by the equation log $k_Q = k_{Q\kappa=0} + 2.0\sqrt{\mu}/(1 + 2.4\sqrt{\mu})$. An unpredicted dependence of the quenching constants on the concentration of fluorescein is observed. This effect, which is caused by the absorption of the fluorescence light in its transit from the body of the solution to the photocell, is eliminated by extrapolation to zero concentration of fluorescein.

5. A new method for measuring the quantum efficiency of fluorescence of dyes in solution has been developed. The quantum efficiency for fluorescein ion is 84 to 85%.

6. Self-quenching of fluorescence results from an encounter between an excited and an unexcited fluorescein ion involving dipole-induced dipole forces.[32] Each encounter results in quenching, *i. e.*, $P(1 - \alpha) \simeq 1$.

7. Iodide ion quenching of fluorescence results from an encounter between an excited fluorescein ion and an iodide ion involving shared-electron and electron-transfer[32] forces. Quenching occurs in, roughly, one out of four encounters, *i. e.*, $P(1 - \alpha) \simeq {}^1/_4$.

---

[32] To be described in a later paper.

NEW YORK, N. Y. RECEIVED OCTOBER 17, 1944

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Moving Boundary Studies on Salt Mixtures

BY L. G. LONGSWORTH

Introduction.—The moving boundary studies previously reported from this Laboratory on salt mixtures[1] were restricted to solutions of two binary salts having a common ion in which the unlike ions have large differences of mobility. Only under these conditions were the boundaries sufficiently sharp to be located with the simple optical arrangements then in use. With the new procedures,[2,3] in which the refractive index gradients in the boundaries are photographed with the schlieren scanning camera during substantially convection-free electrolysis at 0° in the Tiselius cell, this restriction is removed and mixtures of several species of ions having similar mobilities can now be studied. If disturbances due to gravity are avoided, an initially sharp boundary between two such mixtures will generally split, on passage of an electric current, into a number of separate boundaries, each moving at a different rate. This is illustrated by the pattern of Fig. 1. In this experiment a boundary was formed initially between a mixture of lithium chloride and sodium chloride, 0.08 *N* in each, and a mixture of the bromate and iodate of potassium, 0.1 *N* in each. The gradients in this boundary just prior to the passage of the current are indicated by the traced line in Fig. 1. The shaded peaks of this pattern are due to the boundaries that separated on electrolysis.[4]

Although transference data for the salt mixtures have been obtained in the course of this research the chief purpose of the investigation has been to use the new tool for the measurement of the concentration changes accompanying the separation of the boundaries and to show that these changes are in accord with the theory of the process. At the time this investigation was begun the available theory, due to Kohlrausch[5] and Weber,[6] was restricted to ternary ion systems. As more complex systems were studied the need for an extension of the theory became evident. While this work was proceeding, Dr. Vincent P. Dole of these Laboratories developed a general solution, reported in the following paper,[7] for the moving boundary equation and his results have been adapted, where necessary, to the systems described below.

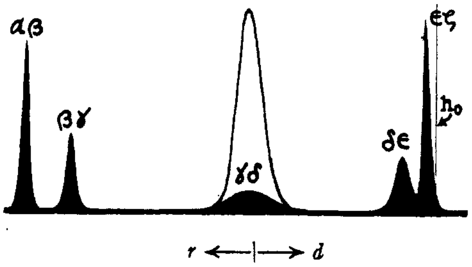

Fig. 1.—Schlieren scanning pattern of the system 0.08 *N* LiCl, 0.08 *N* NaCl–0.1 *N* $KBrO_3$, 0.1 *N* KIO_3.

The work reported here is also proving of value in the interpretation of the electrophoretic patterns of proteins. Although salt and protein ions differ in many respects, the principles underlying the moving boundary studies of these materials are essentially the same. Since the equivalent weights and mobilities of the simple electrolytic ions are well established, mixtures of these ions are better adapted for the experimental tests of the moving boundary theory than are protein mixtures.

Not only do the patterns yield data as to the

---

(1) Longsworth, THIS JOURNAL, **52**, 1897 (1930); **57**, 1698 (1935).

(2) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(3) Longsworth, THIS JOURNAL, **65**, 1755 (1943).

(4) The vertical line, h_0, in this and other patterns of this paper is due to a graduation on the cell from which boundary displacements are measured. Except for the tracing of the initial gradients, the patterns are exactly as photographed.

(5) Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

(6) H. Weber, "Die partiellen Differential-Gleichungen der mathematischen Physik," Braunschweig, 1910, 5th edition, chapter 24.

(7) Dole, THIS JOURNAL, **67**, 1119 (1945).

displacements of the boundaries but the area under a given peak is proportional to the difference of refractive index between the solutions on either side. If these solutions contain only one salt the area affords, as has been shown elsewhere,[8] a measure of the concentration change across the boundary. If, however, the solution of unknown composition contains a mixture of salts, the area must be supplemented by other data.

Experimental

Owing to the relatively large volume available in the Tiselius cell through which a boundary may sweep, it is proving quite practical to remove, as described below, the unknown solution in sufficient quantity for analysis. Otherwise the apparatus and experimental procedure used in the present research have been adequately described in recent papers from this Laboratory.[3,8]

The sampling procedure is as follows. The cell is filled so that the boundary moves in the open side of the channel. After it has undergone a displacement, sufficient to give an accurate value for the transference number, a thin-walled glass capillary is lowered, with the aid of a rack and pinion, into the solution whose composition is desired. This solution is then withdrawn slowly with the aid of the syringe and clock motor arrangement regularly used for shifting the boundary, the capillary being attached to the syringe by means of small bore rubber tubing. During its introduction, some undesired solution enters the capillary. Consequently the tip is first lowered to the level of the upper boundary of the desired layer and the meniscus in the capillary is forced down to this level by injection of air from the syringe before the tip is finally introduced into the layer of solution to be collected.

Owing to the small cross-section of the capillary neither the electrolysis nor the concentration distribution in a boundary is appreciably affected by its presence in the channel. Electrolysis may thus be continued during the sampling. This is of some importance since the solution must obviously be withdrawn slowly in order to avoid any possibility of mixing. Continuation of the electrolysis during this interval also keeps the boundaries sharp and increases the yield. In the present investigation samples from more than one layer of solution in the channel have been collected as just outlined. One is not restricted, therefore, to the relatively insensitive refractometric method used previously nor to a conductometric analysis as in the "balanced boundary" apparatus of Collie and Hartley.[9]

Reagent grade chemicals were used throughout this investigation. The potassium and sodium chlorides were recrystallized, with centrifugal drainage, and fused in air. The iodide, chlorate, bromate and iodate of potassium were dried at 120° after one recrystallization, also with centrifugal drainage. The solutions of these salts were prepared from weighed quantities of both solute and solvent, the volume concentrations at 0° being computed from density data in the "International Critical Tables." In the case of solutions containing more than one solute the contribution of each salt to the density of the mixture was assumed to be the same as in a solution of that salt alone. The salts used only in semi-quantitative experiments were not further purified.

Although the boundary displacements can be determined with adequate precision for the purposes of the present research, the uncertainty in the transference data computed therefrom and reported here is probably somewhat greater than in previous work with the older procedures. Part of this uncertainty is due to the fact that only a few of the experiments were done in duplicate. This could be readily remedied if the additional precision were required. Some uncertainty arises, however, from sources of error, chiefly photographic in origin, that characterize the new procedure. These are the zonal errors of the camera objective, emulsion creep and the ambiguity as to the exact position of the object plane in a field whose depth is 25 mm., which is the length of the light path through the channel. Moreover, the channel itself has been calibrated for total volume only, the uniformity of the cross-section being inferred from the constancy of the boundary velocity under the influence of a constant current. The transference numbers for a solution of a binary salt are, fortunately, subject to the tests that they should be independent of the nature of the following ion and that their sum should be unity. Tests on solutions of potassium chloride indicate that the uncertainty in the transference number from the sources mentioned above is of the order of 0.1%. The advantages of the new procedure far outweigh its defects, however, and the sources of error are being eliminated.

The Moving Boundary Equation.—The distribution, before and after the passage of the current, of the ions in the moving boundary system represented by Fig. 1 is shown diagrammatically in Figs. 2a and 2b, respectively, the patterns as published being turned 90° from the position in which they are obtained. As is indicated in this diagram only the compositions of the two end solutions, α and ζ, that met at the original boundary are known. Within certain limits, determined by the requirement that the lighter solution be on top at each boundary, these solutions may have any arbitrary composition. The compositions of the solutions, $\beta \ldots \epsilon$, formed by the separation of the boundaries are, on the other hand, not arbitrary but depend, in a rather involved manner, upon the concentrations and transference numbers of the ions in the two end solutions. This dependence results from the necessity for conserving mass in each volume element of the system including those in which boundaries may be present. The relation, called the moving boundary equation, between the displacement of a separated, single boundary and the concentrations and transference numbers of the homogeneous solutions on either side is fundamental to the theory of the process and may be derived as follows.

Consider, for example, the boundary, a of Fig. 3, between the solutions α and β that moves against the current, i, through a volume $V^{\alpha\beta}$ to the position b on the passage of one faraday equivalent of electricity. If C_j^α is the equivalent concentration of an anion constituent j in the solution α and C_j^β its concentration in the β solution, the number of equivalents of this species present initially in the volume $V^{\alpha\beta}$ is $C_j^\alpha V^{\alpha\beta}$ and after the passage of the current, $C_j^\beta V^{\alpha\beta}$. Moreover, a number of equivalents of the j ion equal to its transference number, T_j^β, in the β solution simultaneously enter this volume through the plane at a while T_j^α equivalents leave through the plane at b. Conservation of mass for the j ion in the volume $V^{\alpha\beta}$ then gives

$$T_j^\alpha - T_j^\beta = V^{\alpha\beta}\left(C_j^\alpha - C_j^\beta\right) \qquad (1)$$

Similar considerations lead to the same relation

---

(8) Longsworth, This Journal, **66**, 449 (1944).

(9) Collie and Hartley, *Trans. Faraday Soc.*, **30**, 657 (1934).

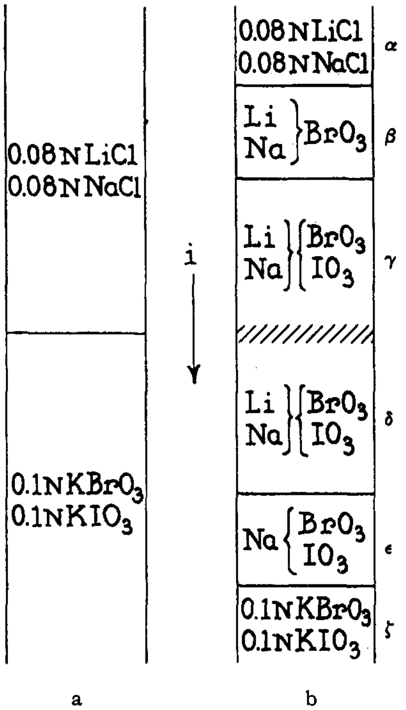

Fig. 2.

when j is a cation if the concentrations are always taken with a sign corresponding to the charge on the ion. The valence of an ion does not, however, enter explicitly into the theory used here since the thermodynamic properties of the ions are not involved. The transference number T_j is always positive. With these conventions $V^{\alpha\beta}$ is positive if the boundary moves with the current and negative if it moves against the current. The boundary displacement, $V^{\alpha\beta}$, is expressed in liters per faraday equivalent since the concentrations are in equivalents per liter. Although the displacement is observed with respect to the apparatus the value to be used in equation 1 is that with respect to the solvent. The observed displacements are thus subject to small corrections for volume changes in the closed side of the apparatus.[8]

Equation 1 is valid for each ion species that may be present in the solutions meeting at the boundary although one of the resulting relations is not independent owing to the requirement of electrical neutrality. This requirement is expressed by the relation $\Sigma C_j = 0$, in which Σ represents a summation over all species present in a given homogeneous solution. The solution, α, into which the boundary moves is called the leading solution whereas that, β, behind the boundary is referred to here as the following solution. It has also been called the adjusted indicator or Kohlrausch solution.

Since the schlieren scanning method records gradients of refractive index it is apparent in Fig. 1, for instance, that actual boundaries are not mathematical planes as is implied in the preceding derivation of the moving boundary equation. In the present research the conditions have, however, been such that the boundaries moved in steady states. In this case equation 1 remains valid if the same property, say the level in the boundary at which the refractive index gradient is a maximum, is always taken as the boundary position. If the boundary is not moving in a steady state care must be exercised in defining its position.[3,7]

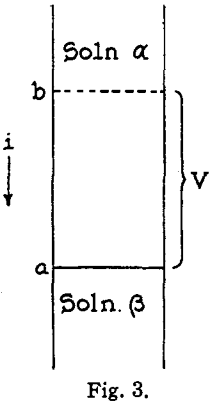

Fig. 3.

Equation 1 will be recognized as a generalization of the relations previously used in work with concentration boundaries,[3] two-salt boundaries[8] and those in which a single salt, BR, is present behind a boundary advancing into a mixture of the two salts, AR and BR.[10] Here, and elsewhere in this paper, A, B, C ... will refer to cations whose mobilities, u, are in the order $u_A > u_B > u_C$ ... while R, S, T ... will indicate anions for which $|u_R| > |u_S| > |u_T|$ .... As implied here the mobilities are taken as signed quantities.

Notation.—Since the use of a diagram, such as that of Fig. 2, to indicate the distribution of ions in a given system is space consuming, a greater compactness and generality may be achieved with the aid of the following notation. The initial boundary will be indicated by separating, with a dash, the symbols for the ions present on the two sides, *i. e.*, the two end solutions. In the system that develops on passage of the current a *moving* boundary is denoted by an arrow while a double colon will be used for the "stationary" or concentration boundary that generally undergoes a very small displacement from the site of the original boundary.

Although the direction in which a boundary moves, relative to the current, depends only on the concentrations and mobilities of the ions in the leading and following solutions, the direction relative to the apparatus also depends upon their densities since the lighter solution must be on top. Consequently it is not possible to specify, for the general case, whether a boundary rises or descends. The direction relative to the current may, however, be indicated by always taking the current as flowing from left to right. A boundary moving with the current will then lie to the right of the stationary boundary whereas one moving against the current will lie to the left. Systems that differ only in the direction in which the boundaries move, *e. g.*, AR ← AS :: AS and BR :: BR → AR, will not be considered as representing different types. In the pattern for any given sys-

---

[10] MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

TABLE I

TRANSFERENCE NUMBER MEASUREMENTS, AT 0°, FOR THE SYSTEM K, Cl, IO_3–KIO_3

1	2	3	4	5	6	7	8	9	10
$-C_{\text{Cl}}^{\alpha}$[a]	$-C_{\text{IO}_3}^{\alpha}$	$-C_{\text{Cl}}^{\gamma}$	$-C_{\text{IO}_3}^{\gamma}$	$-V^{\alpha\beta}$	T_{Cl}^{α}	T_{K}^{α}	$T_{\text{IO}_3}^{\alpha}$	$-C_{\text{IO}_3}^{\beta}$, comp.	$-C_{\text{IO}_3}^{\beta}$, obsd.
0.20	0.00	0.00	0.20	2.529	0.5057	0.4943	0.0000	0.1266	0.1269
.15	.05	.00	.20	2.739	.4109	.5290	.0601	.1449	.1451
.10	.10	.00	.20	2.994	.2994	.5713	.1293	.1636	.1633
.05	.15	.00	.20	3.296	.1648	.6188	.2164	.1813	.1817

[a] The convention regarding ion concentrations as signed quantities accounts for the negative sign when the reference is to an anion.

tem, rising and descending boundaries will be indicated by r and d, respectively, as shown in Fig. 1.

If the total number of ion species, exclusive of those due to the ionization of water, in the two solutions meeting at the original boundary is n, it will be observed that in all of the patterns obtained in this research the number of boundaries that develop on passage of the current is $n - 1$. The n solutions meeting at these boundaries will be denoted, from left to right, by the first n letters of the Greek alphabet. A concentration will, therefore, require two indices, a subscript to denote the species and a superscript to indicate the solution. A double superscript, corresponding to the two adjoining solutions, will serve to identify the boundary to which a property, such as the displacement, refers.

In the notation suggested above the system represented by Fig. 1 would be B, C, R(α) − A, S, T(ζ) for the initial boundary and B, C, R(α) $\leftarrow$ B, C, S(β) $\leftarrow$ B, C, S, T(γ) :: B, C, S, T(δ) $\rightarrow$ B, S, T(ϵ) $\rightarrow$ A, S, T(ζ) after passage of the current. In this instance A refers to the potassium ion K, B = Na, C = Li, R = Cl, S = BrO_3 and T = IO_3.

Gravitational Stability.—The minimizing of convection in the system requires that the lighter solution be on top for each boundary. With ternary ion mixtures it should always be possible to realize this condition, and also to have the boundaries move in steady states, if the other end solution and direction of the current are properly chosen. With the more complex systems studied in this research the ions of one sign have, on the other hand, been selected so that their contributions to the density parallel their mobilities, either directly or inversely. The stability of the system encountered in the electrophoresis of a mixture of proteins dissolved in a buffer solution would appear to indicate that this precaution is not always necessary.[11] This may be due, however, to the small contribution of the protein ions to the conductance of the solution in comparison with their contribution to the density.

Three Ion Systems

The simplest system involving three species, A, R and S, for example, is that, AR–AS, used for the direct determination of transference numbers. On passage of the current this becomes AR(α) $\leftarrow$ AS(β) :: AS(γ) in which the $\alpha\beta$ boundary moving to the left is of the two-salt type. Systems of this kind have already been adequately described.[8]

K, Cl, IO_3 Leading $\leftarrow$ KIO_3 Following.—Results for a three ion system of the type ARS–AS have also been reported previously.[1] A particular case, A = K, R = Cl and S = IO_3, has, however, been studied in this research in order to obtain transference data for mixtures of potassium chloride and potassium iodate that are essential to the interpretation of other systems, AR–ARS and ARS–ARS, involving these same mixtures.

In the case of the $\alpha\beta$ boundary in the system ARS(α) $\leftarrow$ AS(β) :: AS(γ), equation 1 becomes, for the R ion, $T_{\text{R}}^{\alpha} = V^{\alpha\beta}C_{\text{R}}^{\alpha}$ and for the S species $T_{\text{S}}^{\alpha} - T_{\text{S}}^{\beta} = V^{\alpha\beta}(C_{\text{S}}^{\alpha} - C_{\text{S}}^{\beta})$. The displacement, $V^{\alpha\beta}$, thus yields directly the transference number of the R ion in the end solution α of known composition. In order to compute T_{S}^{α} it would also be necessary to determine the concentration, C_{S}^{β}, of the salt AS in the solution, β, formed by the separation of the boundaries, and to know T_{S}^{β} as a function of the concentration in pure solutions of this salt. A better method, however, is to use the relation $T_{\text{S}}^{\alpha} = 1 - T_{\text{A}}^{\alpha} - T_{\text{R}}^{\alpha}$ after T_{A}^{α} has been determined, in an independent experiment, from the displacement of the boundary moving to the right in the four ion system BR $\leftarrow$ BRS :: BRS $\rightarrow$ ARS.

The experimental results for the mixtures of potassium chloride and iodate are recorded in Table I, the first two columns of which give the composition of the leading solution, α. The initial boundary was formed between one of these mixtures and 0.2 N potassium iodate, as indicated in the third and fourth columns of the table. The distribution of gradients at the time electrolysis was begun is shown, for a typical experiment, in Fig. 4a. On passage of the current a boundary, $\alpha\beta$ of Figs. 4b–d, separates and rises in a steady state. The concentration of potassium iodate in the β solution created by the separation of the boundaries is less than 0.2 N and a concentration boundary in this salt remains at $\beta\gamma$ and progressively spreads, mainly by diffusion.

---

(11) The descending β globulin boundary is an exception. Disturbances due to inverted density gradients occur at this boundary as it separates under the influence of the current [Longsworth, Shedlovsky and MacInnes, *J. Exp. Med.*, **70**, 399 (1939)].

The observed displacements, $V^{\alpha\beta}$, *of the* $\alpha\beta$ boundary are given in column 5 of Table III and yield, on substitution in equation 1, the values of T^{α}_{Cl} recorded in column 6. The values of T^{α}_{K}, column 7, were obtained in independent experiments to be described later in this paper. The relation $T^{\alpha}_{\mathrm{IO_3}} = 1 - T^{\alpha}_{\mathrm{Cl}} - T^{\alpha}_{\mathrm{K}}$ was then used to give the values of $T^{\alpha}_{\mathrm{IO_3}}$ recorded in column 8.

Equation 1 for the iodate ion, $T^{\alpha}_{\mathrm{IO_3}} - T^{\beta}_{\mathrm{IO_3}} = V^{\alpha\beta}(C^{\alpha}_{\mathrm{IO_3}} - C^{\beta}_{\mathrm{IO_3}})$, may now be used to compute $C^{\beta}_{\mathrm{IO_3}}$ if $T^{\beta}_{\mathrm{IO_3}}$ is eliminated with the aid of the relation $T^{\beta}_{\mathrm{IO_3}} = 0.3219 + 0.013\ C^{\beta}_{\mathrm{IO_3}}$. This relation was obtained from independent measurements on 0.1 N and 0.2 N solutions of potassium iodate. The computed values of $C^{\beta}_{\mathrm{IO_3}}$ are given in column 9 of Table I. As a check the β solution was removed from the channel and analyzed conductometrically to give the values recorded in column 10. The agreement between the observed and computed values of $C^{\beta}_{\mathrm{IO_3}}$ is comparable with that obtained previously[1] and affords additional confirmation of the validity of the moving boundary equation.

KCl Leading ← K, Cl, IO₃ Following.—If an ion, j, is present in the solution on one side of a boundary but absent in that on the other side it is convenient to describe it as disappearing in the boundary. Since one of the concentrations is then zero, equation 1 becomes $T_j = VC_j$. This relation can, however, be used for the direct determination of T_j only when the boundary moves into a solution in which C_j is known, *i. e.*, an end solution. In the system AR(α) ← ARS(β) :: ARS(γ) no constituent of the leading solution α disappears in the $\alpha\beta$ boundary and its displacement does not yield directly the transference number of any species. This system is of considerable interest, however, since it illustrates an important property of stationary boundaries. Moreover, in work with proteins it is encountered in that side of the moving boundary cell in which a protein ion S, dissolved in a solution of the buffer salt AR, rises into the pure buffer.

In the present case equation 1 becomes, for the R and S species, respectively

$$T^{\alpha}_{\mathrm{R}} - T^{\beta}_{\mathrm{R}} = V^{\alpha\beta}(C^{\alpha}_{\mathrm{R}} - C^{\beta}_{\mathrm{R}}) \qquad (2)$$

$$T^{\beta}_{\mathrm{S}} = V^{\alpha\beta}\, C^{\beta}_{\mathrm{S}} \qquad (3)$$

The quantities C^{α}_{R} and $V^{\alpha\beta}$ may be taken as given and T^{α}_{R} can be determined independently but neither the concentrations nor transference numbers in the β solution are known. Moreover, the relation

$$T_j = C_j u_j / \Sigma C_j u_j \qquad (4)$$

between these quantities and the mobilities, u, indicates that T^{β}_{R} and T^{β}_{S} are functions of both C^{β}_{R} and C^{β}_{S}. It would be possible to determine these functions from transference data, obtained as described in the previous section, for appropriate mixtures of AR and AS. Equations 2 and 3 could then be solved simultaneously for C^{β}_{R} and C^{β}_{S}. Although the transference number of a single binary salt may be readily determined as a function of its concentration, a similar procedure for ternary ion mixtures, in which two independent variables are involved, is not practical.

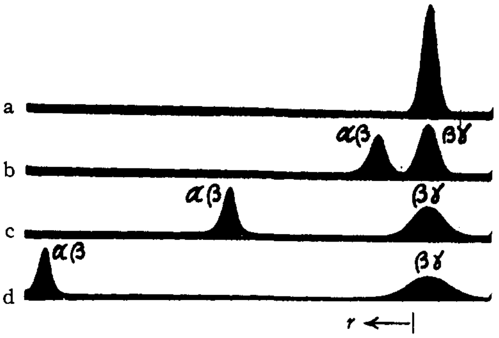

Fig. 4.—Pattern of the system 0.05 N KCl, 0.15 N KIO₃–0.2 N KIO₃.

Equation 4 would give the desired relation if the dependence of the mobilities on the concentrations were known. Since the mobilities occur in this equation as ratios it is essential to know only their values, r_j, relative to that of one species taken as unity. Equation 4 then becomes

$$T_j = C_j r_j / \Sigma C_j r_j = C_j r_j / \sigma \qquad (5)$$

in which the denominator has been designated σ, without a subscript, since it is common to all species in a given solution. With the aid of the assumption that the relative mobilities, r, are constant throughout the system Dole, in the following paper, has obtained a general solution for the moving boundary equation. The results of his analysis will be adapted to the interpretation of the sytem under consideration and to other systems discussed below. The assumption of constant relative mobilities has certain corollaries, however, that should be noted. They are (1) that the transference number of a binary salt is independent of its concentration, (2) that concentration boundaries do not move, with respect to the water, on passage of the current and (3) that ion conductances are additive at finite concentrations. The assumption is only approximately valid, even for aqueous solutions of the strong electrolytes, and it is to be expected, therefore, that computations made with its aid will not agree as closely with experiment as in those systems in which the exact equation 1 may be used.

A simple method for computing the concentrations C^{β}_{R} and C^{β}_{S} in the system AR(α) ← ARS(β) :: ARS(γ) follows from an interesting property of the stationary boundary $\beta\gamma$. For a system in which the relative mobilities are constant, Dole has shown that *all ion species must be present in the same relative proportions on the two sides of the stationary boundary*. It follows from equation 5 that the transference number of each species remains invariant across the stationary boundary,

TABLE II

CONCENTRATION ADJUSTMENTS, AT 0°, IN THE SYSTEMS KCl–K, Cl, IO_3 AND K, Cl, IO_3–K, Cl, IO_3

1 $-C^{\alpha}_{Cl}$	2 $-C^{\alpha}_{IO_3}$	3 $-C^{\gamma}_{Cl}$	4 $-C^{\gamma}_{IO_3}$	5 $C^{\gamma}_{IO_3}/C^{\gamma}_{Cl}$	6 $C^{\beta}_{IO_3}/C^{\beta}_{Cl}$, obsd.	7 $-V^{\alpha\beta}$	8 $-C^{\beta}_{IO_3}$, comp.	9 $-C^{\beta}_{IO_3}$, obsd.	10 $-C^{\beta}_{Cl}$, comp.	11 $-C^{\beta}_{Cl}$, obsd.
0.20	0.00	0.15	0.05	0.333	0.330	1.357	0.0443	0.0433	0.1301	0.1312
.20	.00	.15	.10	1.000	0.982	1.683	.0768	.0772	.0774	.0786
.20	.00	.05	.15	3.000	2.96	2.063	.1049	.1049	.0348	.0355
.15	.05	.05	.15	3.000	2.97	2.246	.1196	.1202	.0404	.0405
.15	.05	.10	.10	1.000	0.992	1.829	.0878	.0887	.0890	.0894
.10	.10	.05	.15	3.000	2.94	2.452	.1355	.1351	.0451	.0460

i. e., $T^{\beta}_{R} = T^{\gamma}_{R}$ and $T^{\beta}_{S} = T^{\gamma}_{S}$ in the present example.

The system studied experimentally was KCl(α) ← K, Cl, $IO_3(\beta)$ :: K, Cl, $IO_3(\gamma)$, in which the end solution, γ, was one of those used as the leading solution, α, in obtaining the data of Table I. The patterns are similar in appearance to those of Fig. 4 and the results are given in the upper half of Table II. The composition, columns 9 and 11, of the β solution, formed by the separation of the boundaries, was obtained by withdrawing this solution from the channel, evaporating a weighed portion to dryness at 80° and drying the residue to constant weight at 120°. The weighed residue was then dissolved and the iodate content determined by titration with thiosulfate, the chloride being obtained by difference. The ratio, $C^{\beta}_{IO_3}/C^{\beta}_{Cl}$ (column 6) of the concentrations determined in this manner is essentially the same as that, column 5, of the γ solution used in forming the initial boundary. It will be noted, however, that the observed values of $C^{\beta}_{IO_3}/C^{\beta}_{Cl}$ are slightly, but consistently, less than the corresponding values of $C^{\gamma}_{IO_3}/C^{\gamma}_{Cl}$. This may be due to experimental error or, what is more likely, to the approximation that the relative mobilities are constant. Within the limits of error imposed by this approximation the β solution holds its constituent ions in the same proportions as in the γ solution but undergoes a dilution, in this instance, at the site of the initial boundary. The results thus afford an experimental confirmation of the theory of stationary boundaries.

Although the value of the ratio, $C^{\beta}_{IO_3}/C^{\beta}_{Cl}$, is governed by the composition of the γ solution, the magnitude of $C^{\beta}_{IO_3}$, and C^{β}_{Cl}, depends upon the properties of the leading solution, α, which the β solution replaces as the $\alpha\beta$ boundary advances. This is shown by the agreement between the observed and computed values for $C^{\beta}_{IO_3}$, columns 8 and 9 of Table II, and for C^{β}_{Cl}, columns 10 and 11. The computed values were obtained from the relations

$$C^{\beta}_{Cl} = C^{\alpha}_{Cl} + (T^{\beta}_{Cl} - T^{\alpha}_{Cl})/V^{\alpha\beta}$$

$$C^{\beta}_{IO_3} = T^{\beta}_{IO_3}/V^{\alpha\beta}$$

Since the β and γ solutions form the stationary boundary the transference numbers T^{β}_{Cl} and $T^{\beta}_{IO_3}$ have, to a close approximation, the same values in the two solutions and are given, therefore, by the appropriate values of T^{α} in Table I. The additional data needed for the computations are the displacements, $V^{\alpha\beta}$, and these are given in column 7.

K, Cl, IO_3 Leading ← K, Cl, IO_3 Following.—The system studied experimentally was K, Cl, $IO_3(\alpha)$ ← K, Cl, $IO_3(\beta)$ :: K, Cl, $IO_3(\gamma)$ and the results are given in the lower half of Table II. As is indicated in this table the end solutions were the same as those for which transference data are given in Table I. Consequently the values of that table may be used to compute, with the aid of equation 1 and the invariance of the transference numbers across the stationary boundary, the composition of the β solution. Although no ion disappears in it, the $\alpha\beta$ boundary moves in a steady state. The patterns are similar, therefore, to those of Fig. 4.

Values of C^{β}_{Cl}, $C^{\beta}_{IO_3}$ and $V^{\alpha\beta}$ may also be computed with the aid of Dole's theory and the relative mobilities given later in Table III. The values thus obtained differ from those observed to about the same extent as do the computed values of Table II. Owing, however, to the approximate nature of the assumption of constant relative mobilities the two methods of computation do not always lead to identical results.

Systems Containing More than Three Ion Species

NaCl-KIO_3.—The simplest example of a four-ion system is afforded by a boundary formed initially between two solutions, each of which contains a single binary salt, with no common ion, *i. e.*, BR–AS. If the salts and relative concentrations have been selected so that the lighter solution remains on top throughout the system, an anion and a cation boundary will separate and advance simultaneously in opposite directions on passage of the current. Moreover, a concentration gradient in the salt formed by the slowest cation and anion will, in general, remain near the site of the original boundary, *i. e.*, BR ← BS :: BS → AR. This is illustrated by the pattern of Fig. 5. A boundary was formed with 0.2 *N* potassium iodate below and 0.2 *N* sodium chloride above and shifted to the center of the channel. The gradients in this boundary immediately

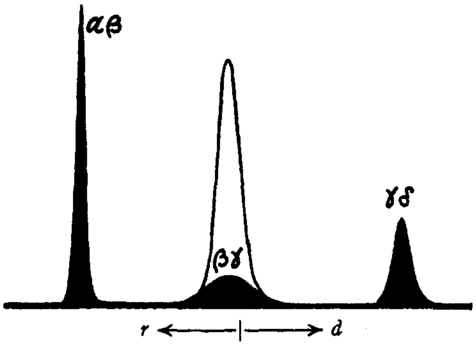

Fig. 5.—Pattern of the system 0.2 *N* NaCl–0.2 *N* KIO_3.

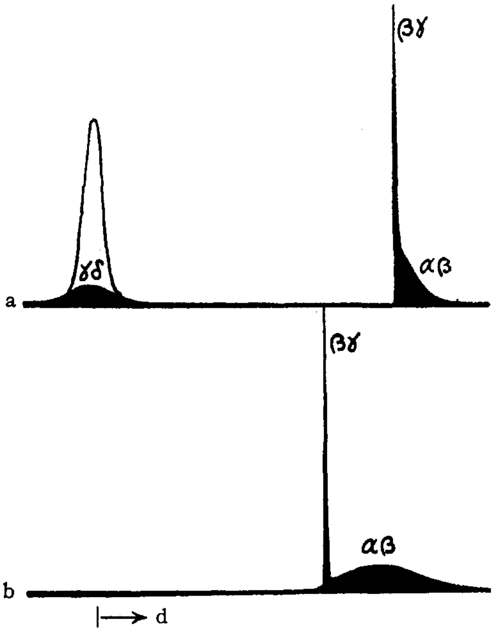

Fig. 6.—Patterns of the system 0.1 *N* NaI, 0.1 *N* NaCl–0.1 *N* $NaCO_2CH_3$.

prior to electrolysis are indicated by the traced line in Fig. 5. On passage of the current this boundary separated into the cation boundary, $\gamma\delta$, descending into the 0.2 *N* potassium iodate solution with a solution of sodium iodate at a concentration of about 0.16 *N* following, the anion boundary, $\alpha\beta$, rising into the 0.2 *N* solution of sodium chloride with 0.14 *N* sodium iodate behind and the concentration boundary, $\beta\gamma$. No new principles are illustrated here since the boundaries $\alpha\beta$ and $\gamma\delta$ are of the two-salt type and are advancing into solutions of known composition. The transference numbers of these solutions may, therefore, be computed directly from the observed displacements. It will be noted that the salt present in the following solutions, *i. e.*, sodium iodate, has been produced electrolytically, a device which may be of practical importance if the solutions are difficult to prepare.

Na, I, Cl–Na Acetate.—Another four-ion system involving no new type of boundary is one in which an ion species, T, follows the ion S as it separates, under the influence of the current, from a mixture of AR and AS, *i. e.*, ARS ← AS ← AT :: AT. An example is afforded by a boundary formed initially between a leading solution 0.1 *N* in both sodium chloride and iodide, and 0.1 *N* sodium acetate in which A = Na, I = R, Cl = S and Ac = T. The patterns obtained in this experiment are shown in Fig. 6, the gradients in the boundary prior to electrolysis being indicated by the traced line of Fig. 6a. This pattern also shows that the separation between the boundaries $\alpha\beta$ and $\beta\gamma$ was incomplete by the time they had descended to the bottom of the channel. Consequently the electrolysis was continued overnight but with solution being injected simultaneously into the cell with the aid of the motor-driven syringe. The boundaries henceforth moved against a countercurrent of solution and were thereby kept in the field of the camera until the separation of the boundaries was essentially complete as shown in Fig. 6b. Of course, the countercurrent soon carried the concentration gradient in sodium acetate, $\gamma\delta$ of Fig. 6a, out of the channel into the top section of the cell and this boundary does not appear in Fig. 6b. Owing to the small difference in conductivity between the original mixture and the solution, β, of sodium chloride being separated therefrom, the leading boundary, $\alpha\beta$ of Fig. 6b, is diffuse. The gradients in the chloride–acetate boundary $\beta\gamma$ were, on the other hand, quite steep. One can compute, from the separation of the boundaries $\alpha\beta$ and $\beta\gamma$ and the quantity of electricity passed, that the iodide ion in the mixture is some 4% faster than the chloride ion.

Two Ions Disappear in the Boundary.—In the determination of T^{α}_{K} for the mixtures of potassium chloride and potassium iodate, Table I, the initial boundary was formed between one of these mixtures, and 0.1 *N* sodium chloride. This system becomes, on passage of the current, NaCl(α) ← Na, Cl, $IO_3(\beta)$ :: Na, Cl, $IO_3(\gamma)$ → K, Cl, $IO_3(\delta)$ and the patterns are similar in appearance to that of Fig. 5. The rising boundary, $\alpha\beta$, is of a type already discussed. The descending boundary, $\gamma\delta$, illustrates, on the other hand, an important property of moving boundaries not previously considered. At this boundary the potassium ion disappears from the leading solution, δ, and the sodium ion disappears from the γ solution. In this respect it is similar to a two-salt boundary and the displacement yields directly the value of T^{δ}_{K}. Unlike a two-salt boundary, however, the two species, Cl and IO_3, are now common to both solutions and it may, therefore, be taken as a generalized example of that class of boundaries in which two species disappear. This represents the special case to which Dole's equation 30 is applicable.

In the present example this equation becomes

$$\frac{C_j^{\gamma}}{C_j^{\delta}} = \frac{r_{Na}(r_j - r_K)}{r_K(r_j - r_{Na})} \qquad (6)$$

TABLE III

RELATIVE ION MOBILITIES, r, AT 0.2 N AND 0°

$r_K = +1.0000$

Ion	Salt	r^a
Cl	KCl	−1.0231
ClO_3	$KClO_3$	−0.8308
IO_3	KIO_3	−0.4691
Na	NaCl	+0.6086

[a] Obtained from transference number measurements on 0.2 N solutions of the salts listed in the second column.

in which j refers either to Cl or to IO_3. Since $r_{\mathrm{Cl}} \neq r_{\mathrm{IO_3}}$, $C^{\gamma}_{\mathrm{IO_3}}/C^{\gamma}_{\mathrm{Cl}}$ should, according to this relation, differ from $C^{\delta}_{\mathrm{IO_3}}/C^{\delta}_{\mathrm{Cl}}$. In one experiment in which $C^{\delta}_{\mathrm{IO_3}}/C^{\delta}_{\mathrm{Cl}}$ was 3.00, analysis of the γ solution gave the significantly different value of 3.32. Computations with the aid of equation 6 and the relative mobilities of Table III gave $C^{\gamma}_{\mathrm{IO_3}}/C^{\gamma}_{\mathrm{Cl}} = 3.30$. For $C^{\delta}_{\mathrm{IO_3}}/C^{\delta}_{\mathrm{Cl}} = 0.333$, the observed and computed values of $C^{\gamma}_{\mathrm{IO_3}}/C^{\gamma}_{\mathrm{Cl}}$ were 0.364 and 0.366, respectively, and for $C^{\delta}_{\mathrm{IO_3}}/C^{\delta}_{\mathrm{Cl}} = 1.00$, $C^{\gamma}_{\mathrm{IO_3}}/C^{\gamma}_{\mathrm{Cl}} = 1.08$ (obsd.) and 1.10 (computed).

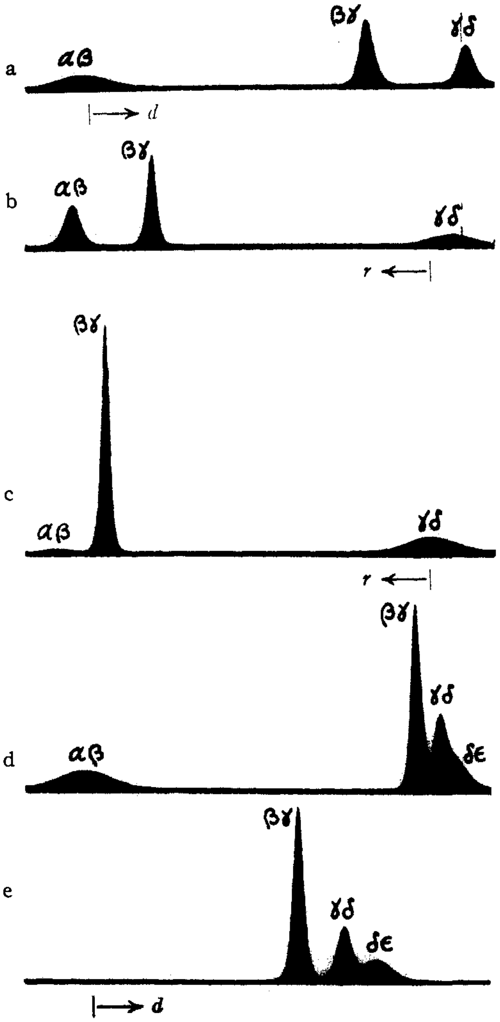

Fig. 7.—Patterns of the systems: (a) 0.2 N LiCl–0.1 N LiCl, 0.1 N NaCl, 0.1 N KCl; (b) 0.08 N KCl, 0.08 N $KBrO_3$, 0.08 N KIO_3–0.2 N KIO_3; (c) 0.08 N KCl, 0.08 N $KClO_3$, 0.08 N KIO_3–0.2 N KIO_3; (d, e) 0.18 N LiCl–0.1 N $MgCl_2$, 0.1 N $CaCl_2$, 0.1 N $BaCl_2$.

These results afford an experimental test of the validity of equation 6 and illustrate a general property of *moving* boundaries. *No two ion species having different mobilities can remain in the same relative proportions across a moving boundary*. This result was first obtained by Svensson[12] and its importance in the interpretation of protein patterns has been emphasized by him. The derivation of the quantitative relation 6 is due, however, to Dole.

One Ion Disappears in the Boundary.—The patterns of Fig. 7 were obtained with the leading solution consisting, in each instance, of a mixture of three binary salts having a common ion. The compositions of the solutions used in forming the initial boundaries are given in the legend for the figure. The system represented by Fig. 7a is LiCl(α) :: LiCl(β) → Li, Na, Cl(γ) → Li, Na, K, Cl(δ), *i. e.*, the fast potassium ion disappears in the leading boundary, $\gamma\delta$, the constituent, sodium, of intermediate mobility disppears at $\beta\gamma$ and the boundary at $\alpha\beta$ is due to a concentration gradient in lithium chloride. In another system, represented by Fig. 7b, the chloride ion disappears in the $\alpha\beta$ boundary, bromate at $\beta\gamma$ and there is a concentration gradient in potassium iodate at $\gamma\delta$. If chlorate is substituted for bromate in this mixture, the leading boundary, $\alpha\beta$ of Fig. 7c, becomes rather faint. In the case of the mixture of magnesium, calcium and barium chlorides, Figs. 7d and 7e, a cation, lithium, is available to follow the slow magnesium ion as it separates from the mixture. An additional, two-salt type of boundary appears, therefore, at $\beta\gamma$ in this five-ion system. Since the boundary separation was still incomplete after they had advanced the length of the channel, Fig. 7d, electrolysis was continued against a countercurrent of solution to obtain the pattern of Fig. 7e.

Since the leading boundary in each of the patterns of Fig. 7 is of a type, ARST ← AST, not previously studied, it is of interest to determine, for a typical case, the concentrations in the β and γ solutions for comparison with values computed with the aid of Dole's theory. The system selected for study was K, Cl, ClO_3, $IO_3(\alpha)$ ← K, ClO_3, $IO_3(\beta)$ ← $KIO_3(\gamma)$ :: $KIO_3(\delta)$, Fig. 7c. The determination, by the usual analytical procedures, of the concentration of both chlorate and iodate in the β solution of this system presented considerable difficulty. Consequently the following moving boundary method was used to determine their ratio, $C^{\beta}_{\mathrm{ClO_3}}/C^{\beta}_{\mathrm{IO_3}}(=\rho^{\beta})$, after which the individual values were obtained refractometrically from the area under the $\alpha\beta$ boundary of Fig. 7c. The method depends upon the fact, already dem-

---

[12] Svensson, *Arkiv Kemi, Mineral. Geol.*, **17A**, No. 14, 1 (1943).

onstrated, that all ions are held in the same proportions across a stationary boundary. Consequently, if the ratio, ρ^{δ}, of chlorate to iodate in the end solution, δ of the system K, Cl, ClO_3, $IO_3(\alpha) \leftarrow$ K, ClO_3, $IO_3(\beta) \leftarrow$ K, ClO_3, IO_3 (γ) :: K, ClO_3, $IO_3(\delta)$ has the same value as that, ρ^{β}, in the solution, β, formed by the separation of the chloride from the mixture, α, the β and γ solutions will be identical and the $\beta\gamma$ boundary will be absent from the system. This condition was found as follows.

With a mixture of potassium chloride, chlorate and iodate, 0.08 N in each, as the α solution, patterns were obtained in which the δ solution was a mixture of potassium chlorate and iodate at a constant total concentration of 0.24 N but in which the ratio, ρ^{δ}, of chlorate to iodate had the values 0.714, 1.00 and 1.40, respectively, in successive experiments. The resulting patterns are shown in Fig. 8. Comparison of these patterns with each other and with that of Fig. 7c, for which $\rho^{\delta} = 0$, shows that the area under the leading boundary, $\alpha\beta$, is independent of ρ^{δ} whereas the area, $A^{\beta\gamma}$, due to the $\beta\gamma$ boundary decreases as ρ^{δ} increases. Consequently, if $A^{\beta\gamma}$ is plotted[13] against a function of ρ^{δ} that permits extrapolation, the value of ρ^{δ} corresponding to $A^{\beta\gamma} = 0$ will be the value of $C^{\beta}_{Cl_3}/C^{\beta}_{IO_3}$ required. As shown in Fig. 9, a plot of $(A_0^{\beta\gamma} - A^{\beta\gamma})/\rho^{\delta}$ *versus* $A^{\beta\gamma}$, in which $A_0^{\beta\gamma}$ is the value of $A^{\beta\gamma}$ for $\rho^{\delta} = 0$, gives a straight line that extrapolates to $\rho^{\delta} = \rho^{\beta} = C^{\beta}_{ClO_3}/C^{\beta}_{IO_3} = 1.55_2$ for $A^{\beta\gamma} = 0$.

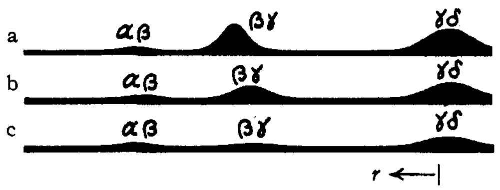

Fig. 8.—Patterns of the systems: (a) 0.08 N KCl, 0.08 N $KClO_3$, 0.08 N KIO_3–0.1 N $KClO_3$, 0.14 N KIO_3; (b) 0.08 N KCl, 0.08 N $KClO_3$, 0.08 N KIO_3–0.12 N $KClO_3$, 0.12 N KIO_3; (c) 0.08 N KCl, 0.08 N $KClO_3$, 0.08 N KIO_3–0.14 N $KClO_3$, 0.10 N KIO_3.

In order to obtain the individual values of $C^{\beta}_{ClO_3}$ and $C^{\beta}_{IO_3}$ there is the additional relation

$$n^{\beta} - n^{\alpha} = k_{KCl}C^{\alpha}_{Cl} - k_{KClO_3}\left(C^{\beta}_{ClO_3} - C^{\alpha}_{ClO_3}\right) - k_{KIO_3}\left(C^{\beta}_{IO_3} - C^{\alpha}_{IO_3}\right) \quad (7)$$

in which k is the equivalent refractive index increment for the salt indicated by the subscript. The difference in refractive index, $n^{\beta} - n^{\alpha}$, between the α and β solutions is proportional to $A^{\alpha\beta}$. Actually the k's vary somewhat with the concentration but here they have been assumed constant and equal to values obtained from refractive index measurements, at 0° and using Hg yellow light, on 0.2 N solutions, *i. e.*, $k_{KCl} = 0.01088$, $k_{KClO_3} = 0.01142$ and $k_{KIO_3} = 0.02774$. Since $n^{\beta} - n^{\alpha} = 0.00004_6$ and $C^{\beta}_{ClO_3}/C^{\beta}_{IO_3} = 1.55_2$, equation 7 then gives the values of $C^{\beta}_{ClO_3}$ and $C^{\beta}_{IO_3}$ listed in column 1 of Table IV. The value of $C^{\gamma}_{IO_3}$ given in this column was obtained from a conductometric analysis of this solution of pure potassium iodate after its removal from the channel.

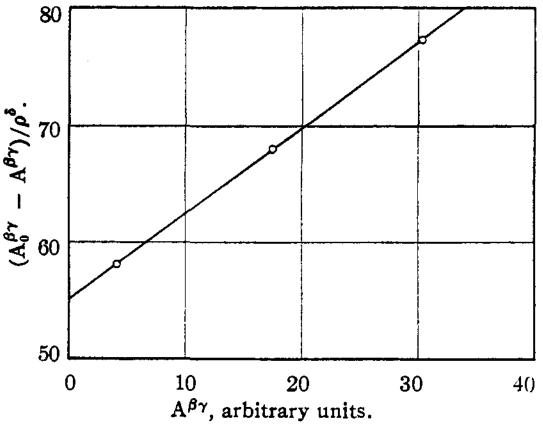

Fig. 9.—Extrapolation plot for the determination of $C^{\beta}_{ClO_3}/C^{\beta}_{IO_3}$ in the system represented by Fig. 7c.

TABLE IV

COMPARISON OF THE OBSERVED AND COMPUTED VALUES FOR THE SYSTEM 0.08 N KCl, 0.08 N $KClO_3$, 0.08 N KIO_3–0.2 N KIO_3

	1 Obsd.	2 Comp.
$-C^{\beta}_{ClO_3}$	0.138_8	0.1412
$-C^{\beta}_{IO_3}$	0.089_1	0.0874
$-C^{\gamma}_{IO_3}$	0.1877	0.1868
$-V^{\alpha\beta}$	2.47_8	2.403
$-V^{\beta\gamma}$	2.15_9	2.147
$n^{\beta} - n^{\alpha}$	0.00004_6	0.000035
$n^{\gamma} - n^{\beta}$	0.00116_6	0.001144
$n^{\delta} - n^{\gamma}$	0.00037_0	0.000366

Using the relative mobilities of Table III and the refractive increments mentioned above, the properties of the system under consideration were computed with the aid of Dole's theory[7] and are given in column 2 of Table IV. In this instance his equation 33 for the α solution becomes

$$\frac{r_{Cl} - r_K}{r_{Cl} - x}\,C^{\alpha}_{Cl} + \frac{r_{ClO_3} - r_K}{r_{ClO_3} - x}\,C^{\alpha}_{ClO_3} + \frac{r_{IO_3} - r_K}{r_{IO_3} - x}\,C^{\alpha}_{IO_3} = 0 \quad (8)$$

This is a quadratic with the two roots, $x_1 = V^{\alpha\beta}\sigma^{\beta} = -0.9298$ and $x_2 = V^{\beta\gamma}\sigma^{\gamma} = -0.5892$. These values are then substituted in the appropriate form of Dole's equation 31. This relation is valid in the present case, since an ion disappears in each of the moving boundaries of the system, and becomes, for the β solution

$$C^{\beta}_{i} = \frac{(V^{\alpha\beta}\sigma^{\beta})(r_{Cl} - r_{i})}{r_{Cl}(V^{\alpha\beta}\sigma^{\beta} - r_{i})}\,C^{\alpha}_{i}$$

---

(13) Although the areas are small they can be determined, using the two-coördinate comparator previously described,[9] with adequate precision.

in which j refers either to ClO_3 or IO_3. A similar relation is then used to obtain $C^{\gamma}_{IO_3}$ after $C^{\beta}_{IO_3}$ has been computed. The boundary displacements are computed from the relations $V^{\alpha\beta} = r_{Cl}/\sigma^{\alpha}$ and $V^{\beta\gamma} = r_{ClO_3}/\sigma^{\beta}$, in which $\sigma = \Sigma C_j r_j$.

In view of the uncertainty, due to the assumption of constant relative mobilities, in the computed data of Table IV the agreement with the observed values is satisfactory. The most serious difference, that in $V^{\alpha\beta}$, merely indicates that at these concentrations ion conductances are not strictly additive. Since $C^{\alpha}_{ClO_3}/C^{\alpha}_{IO_3} \neq C^{\beta}_{ClO_3}/C^{\beta}_{IO_3}$, the results afford another example of the fact that no two species can remain in the same proportions across a moving boundary. It is also of interest that the ion, ClO_3, of intermediate mobility has been preferentially concentrated in the β solution.

No Ion Disappears in the Boundary.—A system that affords a test of the general theory is one containing four ions, 0.15 *N* NaCl, 0.05 *N* $KIO_3(\alpha)$–0.05 *N* NaCl, 0.15 *N* $KIO_3(\delta)$, in which no species disappears in any boundary. The pattern obtained is similar in appearance to that of Fig. 5 and the computed ion concentrations are plotted in Fig. 10 as functions of the height in the moving boundary cell. In making these computations it was necessary to solve, using the relative mobilities of Table III, a quadratic of the form of equation 8 for each of the two end solutions, α and δ, *i. e.*, Dole's equations 33. The roots are $x_1 = V^{\alpha\beta}\sigma^{\beta} = -0.5709$, $x_2 = V^{\gamma\delta}\sigma^{\delta} = 0.8836$, $y_1 = V^{\alpha\beta}o^{\alpha} = -0.8460$ and $y_2 = V^{\gamma\delta}\sigma^{\gamma} = 0.6869$. The computed values for the displacements, $V^{\alpha\beta}$ and $V^{\gamma\delta}$, are then -2.659 and 2.927, respectively, whereas the values observed are -2.658 and 2.936. Moreover, the β and γ solutions were collected, pooled and analyzed for iodate and chloride. The observed and computed values for $C^{\beta\gamma}_{IO_3}/C^{\beta\gamma}_{Cl}$ are 3.14 and 3.15, respectively. The individual ion concentrations plotted in Fig. 10 were computed by substitution of the appropriate $V\sigma$ products into Dole's equation 32

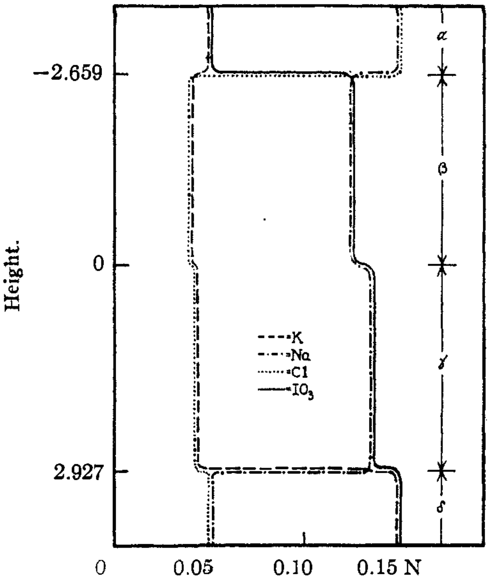

Fig. 10.—Computed distribution of the ion constituents in the system 0.15 *N* NaCl, 0.05 *N* KIO_3–0.05 *N* NaCl, 0.15 *N* KIO_3.

$$C^{\beta}_{i} = \frac{(V^{\alpha\beta}\sigma^{\beta})(V^{\alpha\beta}\sigma^{\alpha} - r_i)}{(V^{\alpha\beta}\sigma^{\alpha})(V^{\alpha\beta}\sigma^{\beta} - r_i)}\, C^{\alpha}_{i}$$

which is applicable to a boundary in which no species vanishes. Although a more complete analysis of this system was not attempted, the above agreement is good evidence that the experimental results are in accord with the theory.

Since no especial precautions were taken in the preparation of the end solutions, the six-ion system represented by Fig. 1 was not studied further. It affords, however, another example of the fact that the number of boundaries that develop on passage of the current is not more than one less than the number of ion species in the two solutions forming the original boundary. Moreover, it is in accord with Dole's conclusion that a system containing p anions and q cations will have $p - 1$ boundaries moving against the current, one stationary boundary and $q - 1$ boundaries moving with the current. In this instance $p = q = 3$.

Discussion

The results presented here afford additional confirmation of the theory of moving boundaries. Together with that theory, a general development of which is given in the accompanying paper by Vincent P. Dole, they furnish a basis for the quantitative interpretation of the patterns obtained in the electrophoretic analysis of protein mixtures. Owing to the large equivalent weight of the protein ions their contribution to the refractive index of the solution is great in comparison with their contribution to the conductance. In the ideal case, approached at high concentrations of buffer salt and low protein concentrations, the transference number of a given protein ion constituent is essentially zero and the gradients in the boundary due to this protein are not superimposed by gradients due to other components. In actual patterns the superimposed gradients are, however, not entirely negligible and introduce errors into the analysis. In earlier papers from this Laboratory[14,15] the existence of buffer salt gradients in a given protein boundary was recognized but gradients due to other protein ions were thought to be negligible. Svensson[12] has correctly pointed out, however, that these latter gradients should also be considered. In so far as the weak electrolyte component of the buffer solution can be neglected and subject to the limitations imposed by the assumption of constant relative mobilities, the theory of moving boundaries is now sufficiently complete and sufficiently

---

(14) Longsworth and MacInnes, THIS JOURNAL, **62**, 705 (1940).

(15) Longsworth, *Chem. Rev.*, **30**, 323 (1942).

well tested experimentally on mixtures of the simple electrolytic ions to permit its application, with confidence, to the quantitative interpretation of the relatively complex protein patterns.

Acknowledgment.—The author is indebted to Dr. D. A. MacInnes of these laboratories for his continued interest in the work and for his care in reviewing the manuscript.

Summary

If disturbances due to convection and gravity are avoided, an initially sharp boundary between two solutions containing n species of ions will split, on passage of an electric current, into not more than $n - 1$ separate boundaries, each of which moves at a different rate. In this research ions differing by only a few per cent. in mobility and systems containing as many as six species have been studied with the aid of the new procedures in which the refractive index gradients in the boundaries are photographed with the schlieren scanning camera during substantially convection-free electrolysis at 0° in the Tiselius cell.

The fundamental moving boundary equation, $\Delta T_j/\Delta C_j = V$, in which V is the displacement of the boundary across which the differences of transference number and concentration of the jth ion are ΔT_j and ΔC_j, respectively, has been shown to be valid for all cases in which accurate transference data were available. The more complex boundary patterns have been interpreted, using the theory of Vincent P. Dole given in the following paper, with the aid of the assumption that relative ion mobilities are independent of the concentration. Within the limits of error imposed by this approximation it has been shown, for all cases studied, that a boundary can remain stationary on passage of the current only if all constituents are in the same relative proportions on either side. At a moving boundary, on the other hand, no two species can exist in the same proportion on the two sides unless their mobilities are identical.

NEW YORK, N. Y. RECEIVED FEBRUARY 28, 1945

[CONTRIBUTION FROM THE U. S. NAVY RESEARCH UNIT AT THE HOSPITAL OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK]

A Theory of Moving Boundary Systems Formed by Strong Electrolytes[1]

BY VINCENT P. DOLE[2]

In an accompanying paper by Longsworth[3] it is shown experimentally that the passage of an electric current across an initially sharp junction between two electrolyte solutions may cause new concentration gradients to form and to move away from the original gradients. From a single original boundary there will thus be formed a system of boundaries. The motion of these boundaries and the composition of the solutions between them may be predicted from the theory to be outlined below, for strong electrolytes, if the disturbing effects of thermal and gravitational convections are avoided. An example of such a system is given schematically in Fig. 1. This system, taken from Fig. 1 of the accompanying paper,[3] involves a total of six different ion species and has one less than that number of boundaries, as will be found to be generally true. Of the five boundaries, one is stationary, indicated by the double bars, and four move, two toward the anode and two toward the cathode, as would be expected from the presence of three anions and three cations. The fact that some of the six ions are missing in the different phases, $\alpha \ldots \zeta$, is not of general significance since a similar system would be developed with all ions present in each phase if the two original solutions, α and ζ, both contained all the ion species.

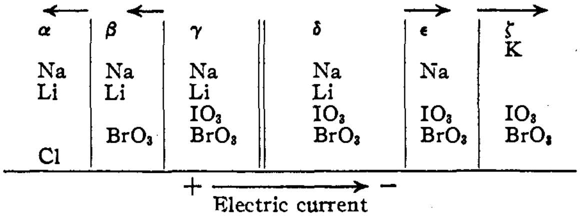

Fig. 1.—Schematic representation of a particular six ion system.

A complete description of such a system—boundary velocities and concentration distributions—could, in principle, be obtained from the compositions of the original solutions with the differential equations of continuity, the electroneutrality requirement and a specification of ion mobilities as functions of composition. This approach to the problem, however, would fail to yield practically useful, general results, because of mathematical complexity and lack of data for specification of the mobilities.

Since the mathematical difficulties arise chiefly in the description of concentration distributions through the boundaries, a simplification is obtained if the continuity equations are developed in a form independent of the particular path by which an ion concentration changes between phases. This device eliminates the complica-

---

[1] The Bureau of Medicine and Surgery does not necessarily undertake to endorse views or opinions which are expressed in this paper.

[2] Lieutenant Commander Medical Corps, United States Naval Reserve.

[3] Longsworth, THIS JOURNAL, **67**, 1109 (1945).